

## Unconventional Ferromagnetic Transition in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

J. W. Lynn,\* R. W. Erwin, J. A. Borchers, Q. Huang,\* and A. Santoro

*Reactor Radiation Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*

J.-L. Peng and Z. Y. Li

*Center for Superconductivity Research, University of Maryland, College Park, Maryland 20742*

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Neutron scattering has been used to study the magnetic correlations and long wavelength spin dynamics of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  in the ferromagnetic regime ( $0 \leq x < \frac{1}{2}$ ). For  $x = \frac{1}{3}$  ( $T_c = 250$  K) where the magnetoresistance effects are largest the system behaves as an ideal isotropic ferromagnet at low  $T$ , with a gapless ( $< 0.04$  meV) dispersion relation  $E = Dq^2$  and  $D_{T=0} \approx 170$  meV  $\text{\AA}^2$ . However, an anomalous strongly field-dependent diffusive component develops above  $\sim 200$  K and dominates the fluctuation spectrum as  $T \rightarrow T_c$ . This component is not present at lower  $x$ . [S0031-9007(96)00221-9]

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The magnetic properties of the doped  $\text{LaMnO}_3$  class of materials have been under very active investigation recently because of the dramatic increase in the conductivity when the spins order ferromagnetically by either lowering the temperature or applying a magnetic field. This huge increase in the carrier mobility originates from a metal-insulator transition that is closely associated with the magnetic ordering. The largest effect is found for the calcium-doped system, and therefore initially we have concentrated on bulk  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  materials [1]. We find that the system is ferromagnetic for  $x < 0.5$ , including the undoped sample, in agreement with recent results for this material [2]. For the  $x = \frac{1}{3}$  doping, where the magnetoresistance anomalies are largest [3], we find that at low  $T$  the magnetic system behaves as an *ideal* isotropic ferromagnet. At elevated temperatures, however, a quasielastic component to the fluctuation spectrum develops for the  $x = \frac{1}{3}$  doping, and becomes the dominant spectral weight as  $T \rightarrow T_c$ . This behavior is in stark contrast to the conventional behavior observed for isotropic ferromagnets and the Ca-doped materials away from  $x = \frac{1}{3}$ . The width of this scattering is proportional to  $q^2$ , indicating that it represents spin diffusion. The correlation length, on the other hand, is anomalously small ( $\sim 10$   $\text{\AA}$ ) and only weakly temperature dependent. These results suggest that this quasielastic component is associated with the electrons becoming localized on the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  lattice, and it is this spin diffusion that drives the ferromagnetic phase transition rather than the thermal population of conventional spin waves.

The diffraction, small angle neutron scattering, and inelastic experiments were all carried out at the NIST research reactor. Because the long wavelength spin dynamics turn out to be approximately isotropic, inelastic measurements on polycrystalline samples may be made in the forward scattering direction [i.e., around the (000) reciprocal lattice point] without loss in generality [4]. All the inelastic measurements reported here were taken on

the BT-9 triple-axis spectrometer, with pyrolytic graphite monochromator, analyzer, and filter. The incident energy was chosen to be 13.7 meV, and horizontal collimations of  $12'-11'-12'-16'$  full width at half maximum (FWHM) were used. The use of polycrystalline samples has the distinct advantage that powder diffraction and profile refinements, which establish the oxygen content and provide detailed crystallographic parameters, may be performed on the same samples. Presently, we have carried out measurements for Ca-doped polycrystalline samples of  $x = 0, 0.15, 0.175, 0.33, 0.44$ , and  $0.5$  made by the usual solid state reaction technique. Our crystallographic studies reveal that there can be orthorhombic, rhombohedral, and monoclinic phases in this range of doping both as a function of temperature and as a function of doping, and these three phases represent subtle structural distortions of the basic perovskite structure. We also observe anomalies in the lattice parameters and structures that are associated with the magnetic ordering, as has recently been reported [5]. However, we believe that these distortions do not by themselves strongly influence the basic spin dynamics, and we will discuss the crystallography in detail elsewhere [6].

For the  $x = \frac{1}{3}$  ( $T_c = 250$  K) material that is of primary interest here the crystal structure is orthorhombic ( $Pnma$ ) over the entire range of the temperature and field we have explored, while for temperatures well below  $T_c$  the magnetic system behaves as an ideal isotropic ferromagnet. Thus, in the long wavelength (hydrodynamic) regime, the magnetic excitations are expected to be conventional spin waves with a dispersion relation  $E = \Delta + D(T)q^2$ , where  $\Delta$  represents the spin-wave energy gap and the spin stiffness coefficient  $D(T)$  is directly related to the exchange interactions [7]. Figure 1(a) shows a typical magnetic inelastic spectrum collected at 200 K and wave vector  $q = 0.07$   $\text{\AA}^{-1}$ . A flat background of 9 counts plus an elastic incoherent nuclear peak of 647 counts, measured at 14 K, have been subtracted from these data. We see that the spectrum is dominated by spin waves

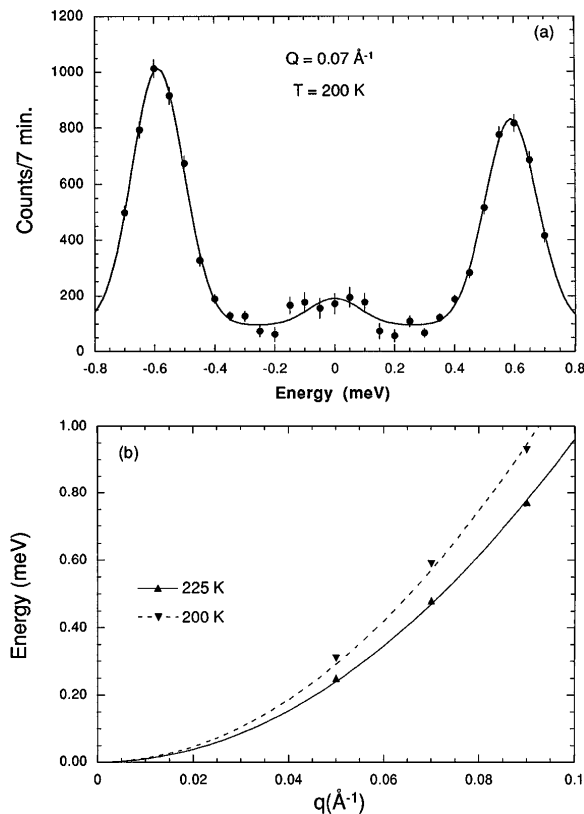


FIG 1. (a) Inelastic scattering below  $T_C$  for  $x = \frac{1}{3}$  at a wave vector of  $0.07 \text{ \AA}^{-1}$ . The spectrum is dominated by the spin waves in energy gain ( $E < 0$ ) and energy loss ( $E > 0$ ). (b) Quadratic spin-wave dispersion relation with a negligible spin-wave gap, as expected for an isotropic ferromagnet.

observed in energy gain ( $E < 0$ ) and energy loss ( $E > 0$ ). Similar data were obtained at a series of wave vectors and temperatures, and Fig. 1(b) shows the measured spin-wave dispersion relation at two different temperatures. We see that the dispersion relation is indeed quadratic in  $q$ . At low temperature the widths of the spin waves are solely instrumental in origin, and this demonstrates that the dispersion relation is indeed isotropic in  $\vec{q}$ ; any significant anisotropy would reveal itself as an apparent intrinsic linewidth in these powder measurements [8]. This isotropy in the dispersion relation indicates that the net exchange interactions do not depend on the direction in the crystal to a good approximation. We also note that any spin-wave gap  $\Delta$  is too small ( $< 0.04 \text{ meV}$ ) to be determined in these measurements, which is consistent with high resolution measurements on a Sr-doped single crystal [9]. The energy gap  $\Delta$  may be simply interpreted as the cost in energy to perform a uniform rotation of all the spins from the easy spin direction in the crystal into a “hard” direction. The very small value of  $\Delta$  in the present system indicates that this is a “soft” ferromagnet, comparable to very soft amorphous ferromagnets [4]. Finally, we note that the low temperature value of the spin stiffness constant  $D(0)$  is  $\sim 170 \text{ meV \AA}^2$ . This gives a ratio of  $D/kT_C \approx 7.9 \text{ \AA}^2$

that is quite large, as might be expected for an itinerant electron system [10].

As we raise the temperature towards  $T_C$  for a conventional ferromagnet that exhibits a second-order phase transition, we expect the intensity of the spin-wave scattering at each  $q$  to increase rapidly as the thermal population increases according to the Bose factor. This thermal population effect is further enhanced because of the renormalization (softening) of the spin-wave energy, with  $D(T)$  expected to exhibit power law behavior and  $D(T \rightarrow T_C) \rightarrow 0$ . The data in Fig. 2(a) show that the spin waves do soften with increasing temperature. However, they do not collapse as  $T \rightarrow T_C$ , with  $D(T_C)$  only about half of its low temperature value. The measured (Bragg peak) magnetization as a function of temperature is shown in Fig. 2(b) for comparison. This is rather typical of a magnetization curve, and gives  $T_C \approx 250 \text{ K}$ . However, the data are not the same on warming and cooling, but exhibit an irreversibility of 5 K. This irreversibility clearly demonstrates that the magnetic transition is not a continuous, second-order transformation. We also found that in the ordered phase the time scale for the magnetic intensity to equilibrate is significant ( $\sim 10$ – $20 \text{ min}$ ), which provides further evidence that the paramagnetic

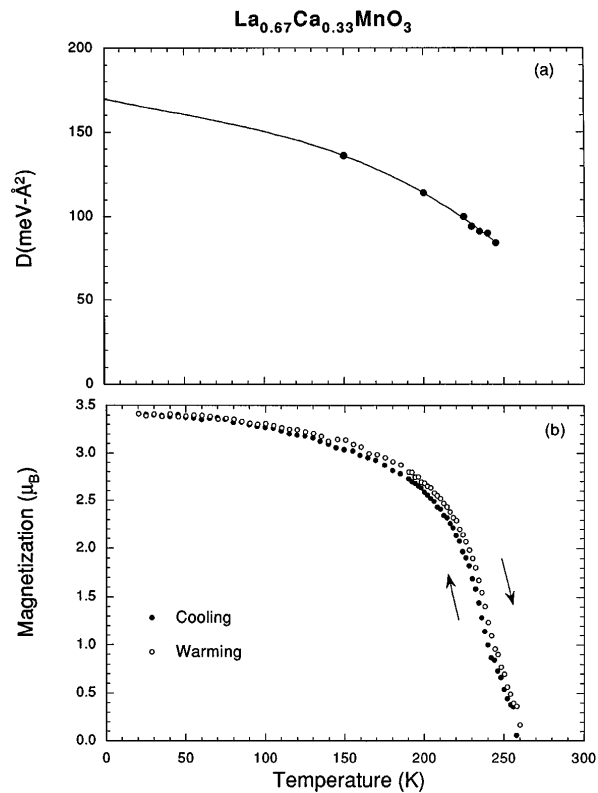


FIG. 2. (a) Spin stiffness coefficient  $D$  in  $E = Dq^2$  as a function of temperature.  $D$  does not vanish at the ferromagnetic transition temperature, in contrast to the behavior of a conventional ferromagnet. The solid curve is a guide to the eye. (b) Magnetization versus  $T$  obtained from Bragg scattering. The data appear continuous and indicate  $T_C \approx 250 \text{ K}$ , but the scattering is not reversible on warming and cooling.

↔ ferromagnetic transition is not continuous. At lower  $x$  we did not observe these long time scales, and the irreversibility in the data was only 2 K or less.

The spin dynamics associated with the phase transition for  $x = \frac{1}{3}$  are also anomalous as shown in Fig. 3, where we have plotted the magnetic scattering at  $q = 0.07 \text{ \AA}^{-1}$  for temperatures of 225 and 235 K. These data were taken with the same instrumental conditions as the data shown in Fig. 1(a) and may be directly compared. At 225 K we see that the spin waves have softened somewhat in energy (shifting towards  $E = 0$ ), but the most dramatic change is the appearance of a quasielastic component comparable in intensity to the spin waves. At 235 K the spin waves clearly renormalize to lower energies (and broaden), but the central peak now dominates the fluctuation spectrum. For typical isotropic ferromagnets such as Ni [11], Co [12], Fe [13], or amorphous materials [4], any quasielastic scattering below  $T_C$  is too weak and broad to be observed directly in the data, and can only be distinguished by the use of polarized neutron techniques [14]. This is also the case for smaller concentrations of Ca where we have investigated the dynamics.

The data in Fig. 3 show that the observed width of the central peak is broader than the spin waves, and this indicates that there is an intrinsic width to the quasielastic scattering. The shape of the scattering can be fit rather well by a Lorentzian line shape for all three peaks, and Fig. 4(a) shows the deconvoluted energy width  $\Gamma$  for the quasielastic peak as a function of  $q$  at  $T = 240 \text{ K}$ . The quadratic dependence on  $q$  ( $\Gamma = \Lambda q^2$ ) demonstrates that this scattering originates from a diffusion mechanism [7], with an effective diffusion constant  $\Lambda = 30 \text{ meV \AA}^2$  at this temperature. The  $q$  dependence of the energy-integrated intensity provides a measure of the associated length scale for this diffusion, and from these data, as

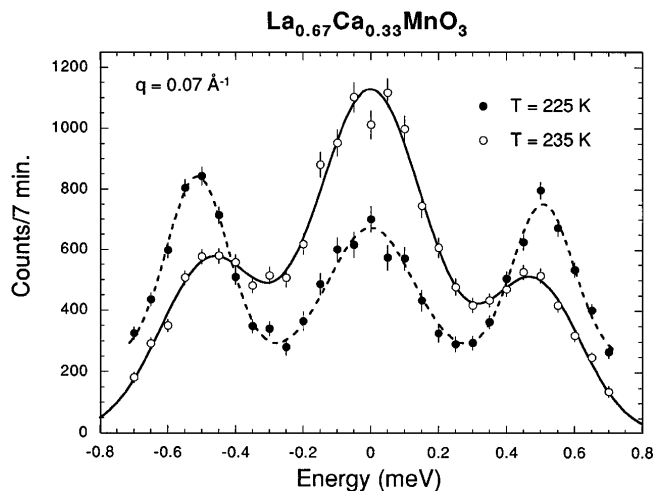


FIG. 3. Inelastic spectrum at 225 and 235 K for  $q = 0.07 \text{ \AA}^{-1}$ . The spin waves soften in energy with increasing temperature, but the dominant effect is the development of the strong quasielastic scattering component in the spectrum.

well as from preliminary small angle scattering (SANS) measurements, we obtain a very short length scale of  $\sim 12 \text{ \AA}$  at this temperature. The SANS data also reveal that as  $T \rightarrow T_C$  from high  $T$  the correlation length  $\xi$  is only weakly temperature dependent and does not diverge, with  $\xi_{T_C} \sim 10 \text{ \AA}$ . The short length scale and weak temperature dependence suggests that this quasielastic scattering originates from electron diffusion on the Mn sublattice.

We now turn to the temperature dependence of the intensities of scattering as shown in Fig. 4(b). We see that the spin-wave intensity does start to increase with increasing temperature as expected, but above  $\sim 200 \text{ K}$  the nature of the spin dynamics begins to change. In particular, as  $T \rightarrow T_C$  the spectral weight for the spin-wave excitations actually starts to *decrease*, while the weight for the spin-diffusion component rapidly increases. This spin-diffusion component strongly dominates the fluctuation spectrum near  $T_C$ , in marked contrast to conventional ferromagnets. We have also found that the

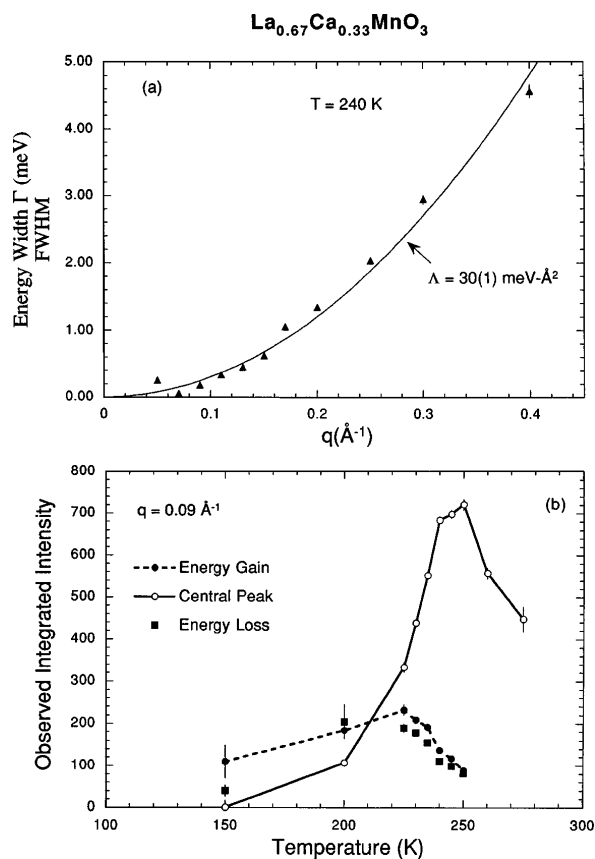


FIG. 4. (a) Width in energy  $\Gamma$  versus  $q$  for the quasielastic scattering at 240 K. The quadratic dependence on  $q$  indicates that this scattering originates from spin diffusion. (b) Integrated intensities versus temperature for the spin waves and spin-diffusion scattering at  $0.09 \text{ \AA}^{-1}$ . The spin-wave intensity actually decreases as  $T$  approaches  $T_C$ , while the quasielastic scattering becomes an order of magnitude stronger than the spin-wave scattering. Above  $T_C$ , all the scattering in this range of  $q$  is quasielastic.

spectral weight for this spin-diffusion component can be shifted back into the spin waves by the application of magnetic fields of a few tesla, which is the field regime associated with the colossal magnetoresistance effects [3]. The appearance of this quasielastic scattering for  $x = \frac{1}{3}$  contrasts with the behavior we find at  $x = 0.15, 0.175$ , for example, where the magnetic fluctuation spectrum below  $T_C$  is dominated by spin-wave excitations and it is difficult to discern any distinct quasielastic component (as in conventional ferromagnets).

It is therefore clear that this ferromagnetic phase transition in the  $x = \frac{1}{3}$  material is not driven by the thermal excitation of spin waves as for a conventional ferromagnetic phase transition, but rather is driven by this spin-diffusion mechanism. The short length scale associated with this diffusion suggests that this component originates from the electronic hopping from site to site on the  $\text{Mn}^{3+}/\text{Mn}^{4+}$ . The strong enhancement of this component of the magnetic fluctuation spectrum for  $x$  where the colossal magnetoresistance effects are observed provides a direct link between the ferromagnetic phase transition and the metal-insulator transition associated with the electronic diffusion and localization that occur in the same temperature and field regime. A straightforward interpretation of the data is that the spin-wave excitations and spin-diffusion component coexist, with a uniform magnetization throughout the sample. Another interpretation of our results, though, is that the system is inhomogeneous, consisting of two distinct phases. The phase preferred at low  $T$  (or high  $H$ ) is an ordered ferromagnet with metallic conductivity, a finite magnetization, and well-defined spin waves [ $D(T_C) \sim \frac{1}{2}D(0)$ ], while the high- $T$  phase is a paramagnet where the electrons diffuse on a short length scale. As the temperature is increased towards  $T_C$  the fraction of these two phases would then change as the ferromagnetic phase converts to the paramagnetic phase in a discontinuous fashion. We tend to favor this latter interpretation since it is also consistent with the lattice anomalies and magnetic irreversibilities we have observed for  $x = \frac{1}{3}$ . However, in the small- $q$  regime explored in the present measurements we do not see any direct evidence in the dynamics of the coupling of the magnetic system to the lattice [15].

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\*Also at the University of Maryland, College Park, MD 20742

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